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(54) Method of fabricating a superconductive body, and apparatus and systems comprising the body.

(57) Articles comprising a quantity of superconductive oxide material can be fabricated by a process that comprises melting of part of an oxide precursor material, with resultant directional resolidification. Exemplary embodiments comprise zone melting and movement of the hot zone through the precursor material. The method can result in superconductive material having improved properties, e.g., higher critical current, as compared to prior art oxide superconductors. An exemplary technique for melting of the precursor material is zone melting.

FIG. 8

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METHOD OF FABRICATING A SUPERCONDUCTIVE BODY, AND APPARATUS AND SYSTEMS COMPRISING THE BODY

Field of the Invention

This invention pertains to methods of producing superconductive bodies, and to apparatus and systems comprising a superconductive body produced by such a method.

Background of the Invention

From the discovery of superconductivity in 1911 to the recent past, essentially all known superconducting materials were elemental metals (e.g., Hg, the first known superconductor) or metal alloys or intermetallic compounds (e.g., Nb_3Ge, probably the material with the highest transition temperature T_c known prior to 1986).

Recently, superconductivity was discovered in a new class of materials, namely, metal oxides. See, for instance, J. G. Bednorz and K. A. Muller, Zeitschr. f. Physik B - Condensed Matter, Vol. 64, 189 (1986), which reports superconductivity in lanthanum barium copper oxide.

The above report stimulated worldwide research activity, which very quickly resulted in further significant progress. The progress has resulted, inter alia, to date in the discovery that compositions in the Y-Ba-Cu-O system can have superconductive transition temperatures T_c above 77K, the boiling temperature of liquid N_2 (see, for instance, M. K. Wu et al, Physical Review Letters, Vol. 58, March 2, 1987, page 908; and P. H. Hor et al, ibid, page 911). Furthermore, it has resulted in the identification of the material phase that is responsible for the observed high temperature superconductivity, and in the discovery of composition and processing techniques that result in the formation of bulk samples of material that can be substantially single phase material and can have T_c above 90K (see, for instance, R. J. Cava et al, Physical Review Letters, Vol. 58(16), pp. 1676-1679).

The excitement in the scientific and technical community that was created by the recent advances in superconductivity is at least in part due to the potentially immense technological impact of the availability of materials that are superconducting at temperatures that do not require refrigeration with expensive liquid He. Liquid nitrogen is generally considered to be one of the most advantages cryogenic refrigerants, and attainment of superconductivity at or above liquid nitrogen temperature was a long-sought goal which until very recently appeared almost unreachable.

Although this goal has now been attained, there still exist barriers that have to be overcome before the new "ceramic" superconductors can be effectively utilized in technological applications. In particular, the ceramic high T_c superconductive materials are relatively brittle. Development of techniques for fabricating the brittle compounds into bodies of desirable size and shape (e.g., wires or tape), and of techniques for improving the strength and/or other mechanical properties of ceramic superconductive bodies, is an urgent task for the technical community. Furthermore, techniques for increasing the critical current density J_c of bodies formed from superconductive compounds are also of great significance.

For a general overview of some potential applications of superconductors see, for instance, B. B. Schwartz and S. Foner, editors, Superconductor Applications: SQUIDS and MACHINES, Plenum Press 1977; and S. Foner and B. B. Schwartz, editors, Superconductor Material Science, Metallurgy, Fabrications, and Applications, Plenum Press 1981. Among the applications are power transmission lines, rotating machinery, and superconductive magnets for, e.g., fusion generators, MHD generators, particle accelerators, levitated vehicles, magnetic separation, and energy storage, as well as junction devices and detectors. It is expected that many of the above and other applications of superconductivity would materially benefit if high T_c superconductive material could be used instead of the previously considered relatively low T_c materials.

The art has followed three approaches in producing ceramic superconductive compound bodies. One approach comprises providing the desired compound in powder form, producing a bulk body from the powder by any appropriate technique (e.g., cold or hot pressing in or through a die of desired size and shape, or forming a slurry and producing a tape therefrom by the doctor blade technique) and heat treating the resulting body. See U. S. Patent application, Serial No. 036,168, filed April 6, 1987 for E. M. Gyorgy et al, titled "Apparatus Comprising a Ceramic Superconductive Body, and Method for Producing Such a Body." The heat treatment invariably comprises treatment at a relatively high temperature that is intended to produce sintering of the powder particles, followed typically by optimization of the oxygen content of the material. The thus produced superconductive bodies typically are relatively porous (e.g., about 85% dense, depending on processing conditions). Furthermore, powder particles may not always be

in intimate contact with their neighbors. The presence of voids and/or poor contact between particles is thought to be a possible reason for the relatively low strength and critical current of bodies produced from superconductive oxide powder by ceramic processing techniques.

A recently filed U.S. patent application (Serial No. 046,825, filed May 5, 1987 for S. Jin et al) discloses that some properties of superconductive compound bodies (e.g., their mechanical strength) can be improved by admixture of an appropriate metal powder (e.g., Ag) to the superconductive powder.

The second approach typically comprises forming a "perform" by introducing a quantity of superconductive compound powder into a tubular normal metal body, reducing the cross section of the preform by, e.g., drawing through a die (or dies) or rolling, until the desired wire or ribbon is produced. The wire or ribbon is then typically wound into a coil or other desired shape, followed by a sintering treatment and, possibly, an oxygen content-optimizing treatment. Two recent U.S. patent applications (Serial No. 036,160, filed April 6, 1987 for S. Jin et al, and Serial No. 046,825, filed May 5, 1987 for S. Jin et al) disclose techniques for forming metal-clad high T_c superconductive bodies. Such bodies typically are also relatively porous, and have the relatively low T_c associated with high T_c superconductors produced by ceramic processing techniques.

The third approach to forming superconductive compound bodies comprises depositing a thin layer of the superconductive compound on an appropriate substrate. Deposition can be by any appropriate method, e.g., electron beam evaporation, sputtering, or molecular beam epitaxy. Another recently filed U.S. patent application (Serial No. 037,264, filed April 10, 1987 for C. E. Rice) discloses that thin superconductive films can be produced by forming a solution on a substrate, and heat treating the thus formed thin layer. The high T_c compound thin films known to the art are thought to be substantially 100% dense, and at least in isolated instances relatively high critical currents have been observed in such layers.

In view of the fact that technologically significant superconductive wires, ribbons, and other bodies have to be able to carry relatively high current densities and to be able to withstand relatively large forces, fabrication methods that can result in high T_c superconductive bodies having improved properties (including higher J_c and, typically, greater strength and thermal conductivity) would be of considerable significance. This application discloses such a method.

Definitions

The Ba-cuprate system herein is the class of oxides of nominal general formula $Ba_{2-x}M_{1-y}X_{x+y}Cu_3O_{9-\delta}$, where M is one of Y, Eu, or La, and X is one or more optional element different from Ba and M and selected from the elements of atomic number 57-71, Sc, Ca, and Sr. Typically x+y is in the range 0-1 (with Ba and M being at least 50% unsubstituted), and typically $1.5 < \delta < 2.5$. In a particular preferred subclass of the Ba-cuprate system $0 \leq y \leq 0.1$, with X being one or more of Ca, Sr, Lu and Sc. For further examples see D. W. Murphy et al, Physical Review Letters, Vol. 58(18), pp. 1888-1890 (1987).

A slightly different definition of the Ba-cuprate system that has also been used is based on the general formula $Ba_{2-y}(M_{1-x}M'_x)_{1+y}Cu_3O_{9-\delta}$, where M and M' are chosen from Y, Eu, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, Lu, La, Sc, Sr or combinations thereof, with typically $0 \leq x \leq 1, 0 \leq y \leq 1$, and $1 < \delta < 3$. See, for instance, U.S. Patent application Serial No.118,497, titled "Method of Producing Metal Oxide Material, and of Producing a Superconductive Body Comprising the Material", filed on November 9, 1987 for S. Jin, M. Robbins, and R. C. Sherwood.

The La-cuprate system herein is the class of oxides of nominal general formula $La_{2-x}M_xCuO_{4-\epsilon}$, where M is one or more divalent metals (e.g., Ba, Sr, Ca), and $x \leq 0.05$, and $0 \leq \epsilon \leq 0.5$.

A "normal" metal herein is a metal that does not become superconductive at temperatures of technological interest, typically at temperatures of 2K and above.

A body herein is "relatively dense" if at least a major part of the body has a density that is at least 90% of the theoretical density of the material in the part of the body. Preferably the density in the part of the body is greater than 95 or even 99% of the theoretical density. The theoretical density of $Ba_2YCu_3O_7$ is about 6.4g/cm^3, and the density of sintered $Ba_2YCu_3O_7$ bodies (heat treated to optimize the superconductive properties) typically is no more than about 5.5g/m^3 (about 85% of theoretical).

Summary of the Invention

We have discovered that superconductive compound (e.g., Ba-cuprate and La-cuprate) bodies can be produced by a process that comprises melting a quantity of precursor material, and cooling at least a portion of the melt such that a solid body of a desired shape (e.g., a filament) results, with at least a substantial portion of the superconductive body having a density greater than about

90% of the theoretical density of the superconductive compound. The inventive method typically further comprises heat treating the solid body in an oxygen-containing atmosphere so as to impart the desired superconductive properties to the body. For instance, at least for an exemplary member of the Ba-cuprate system (nominal composition $Ba_2YCu_3O_7$) an appropriate exemplary heat treatment comprises maintaining the body at a temperature in the approximate range 859-950°C in an oxygen-containing atmosphere for a period of time in the range 1-48 hours, followed by slow cooling. Although not a requirement, in many cases it will be desirable for the inventive method to be carried out such that the resulting body consists substantially of single phase material.

The inventive technique represents a complete departure from prior art processing of bulk Ba-cuprate and La-cuprate material. These materials, which are ceramics, have in the past been processed by ceramic techniques. In general, ceramic processing techniques do involve high temperature treatment (e.g., sintering). However, standard high temperature processing of ceramic materials is carried out at temperatures below the melting point of the material, and melting of ceramic material is, to the best of our knowledge, not used in the production of any commercially significant ceramic.

All the currently known high T_c ceramic superconductive compounds are either La-cuprates or Ba-cuprates. Both these systems have complicated phase diagrams, with single phase-based superconductivity occurring only in relatively narrow compositional ranges. Due to these circumstances conventional theory suggests that solidification of material from a melt of composition corresponding to that of the superconductive phase will result in decomposition into a multiphase material that is not superconductive, or only partly superconductive at "high" temperatures (e.g., at or above 77K).

Thus, not only is processing that involves melting of the ceramic material not within the normal repertoire of ceramicists but, based on the phase diagram of the prototypical Ba-cuprate $YBa_2Cu_3O_{9-\delta}$), a man skilled in the art has good reason for not melt-processing the material.

However, we have made the unexpected discovery that it is possible to produce superconductive material by a method that comprises cooling from the single phase liquid region (exemplarily sufficiently rapid cooling such that phase separation is substantially avoided or minimized), or that comprises cooling from the solid + liquid region of the phase diagram.

After solidification of the melt a variety of treatments may be applied. For instance, the sample can be maintained in O_2 at a temperature between the solidus and that of any solid state transformation (if such a transformation exists) for a relatively long period (e.g., 1-24 hrs) to facilitate homogenization and/or grain growth, followed by a slow cool (possible with intermediate soaks) in O_2 to room temperature. On the other hand, the solidified sample can be cooled slowly (typically in O_2) to room temperature, with a later homogenization treatment in O_2 at a temperature relatively close to but below the solidus (exemplarily 1-24 hours at 850-950°C). Intermediate treatment schedules are also possible.

In a currently preferred embodiment the melt is cooled relatively rapidly (exemplarily within about 1-600 seconds) from the liquid region of the phase diagram to an intermediate temperature slightly below the solid + liquid region (exemplarily 10-100°C below the solidus and above any solid state phase transition temperature that may be present in the system), followed by a heat treatment that favors the growth of crystallites of the superconductive phase and avoids thermal shock and the consequent formation of microcracks. If the cooling from the melt is carried out too slowly (e.g., within more than about 10 minutes) an unacceptable amount of phase separation (typically more than about 15% by volume of non-superconductive phase) is likely to occur, and if the cooling is carried out too quickly (e.g., within less than about 1 second), microcracks may form. The details obviously will depend, inter alia, on the amount and shape of the material that is to be solidified. The heat treatment of the solidified material exemplarily comprises a slow cool (e.g., furnace cool, 1-100 hours) in O_2 to about room temperature, and optionally comprises a soak in O_2 at the intermediate temperature, or some other elevated temperature. Exemplarily, a melt of composition $YBa_2Cu_3O_x$ ($x \sim 7$) is maintained under O_2 at about 1300°C for about 5 minutes, the melt is then rapidly cooled in O_2 to about 950°C, followed by a furnace cool in O_2 to room temperature. The resulting material typically has spherulitic microstructure, with many grains being oblong, having a long axis of about 20-200 µm. The material typically is substantially single phase, essentially 100% dense, and has T_c of about 92K and J_c of more than about 2000 A/cm^2 (at 77K, with $H=0$).

In a further exemplary embodiment the material is heated to a temperature in the solid + liquid region of the phase diagram, optionally maintained in that region under O_2 for a period sufficient to result in establishment of approximate phase equilibrium (e.g., 5 second - 5 hours), followed by a relatively slow cool (e.g., furnace cool 1-24 hours) in O_2 to about room temperature (with an optional soak or soaks at one or more temperatures below the solidus not excluded). Exemplarily, a melt of composition $YBa_2Cu_3O_x$ is maintained at 1030°C for about 1 hour and furnace cooled. The

resulting material typically has predominantly spherulitic microstructure, comprises, in addition to the superconducting phase, crystallites of nominal composition $Y_2BaCu_3O_5$ and also copper oxide and barium oxide. The material typically is essentially 100% dense, and has exemplarily T_c of about 92K and J_c of about 1700A/cm^2 (at 77K, with H=0).

As is apparent from the above cited properties, superconductive bulk samples produced according to the invention can have higher J_c (including substantially greater J_c in a magnetic field) than prior art bodies. Furthermore, bodies produced according to the invention typically also can have greater mechanical strength and greater thermal conductivity.

The known superconductive oxides are relatively reactive and can be expected to interact with most common crucible materials. Consequently, it may be advantageous to use a crucible-free method of melting of the starting material, or to melt the starting material in a crucible that provides a particular constituent to a starting material that is initially deficient in that constituent. For instance, Y-poor Ba-Y-Cu oxide starting material can be melted in a Y_2O_3-lined crucible, with the starting composition, melt temperature, soak time, etc. chosen such that the solidified material has the desired 1:2:3 ratio of Y:Ba:Cu.

The inventive method, or obvious variations thereof, can be used in conjunction with the known superconductive compounds, namely, the members of the Ba-cuprate system and of the La-cuprate system. There have been reports that, for instance, in some samples of nominal composition $Ba_2Y_1Cu_3O_{6.9}$ indications of superconductivity were detected at temperatures above 100K. If these reports are correct, then it is likely that an unidentified phase of the material becomes superconductive at a temperature above 100K. We consider it likely that the inventive method, or an appropriate extension thereof, could be used to produce superconductive bodies that comprise the alleged high T_c phase, should the phase exist. Furthermore, the inventive method, or an appropriate extension thereof may even likely be useful in connection with making superconductive bodies from non-cuprate superconductive compounds (e.g., nitrides, sulfides, hydrides, carbides, fluorides, and chlorides), should such non-cuprate superconductive compounds exist. However, in the remainder of this application we will generally only refer to cuprate superconductors, in particular, to the Ba-cuprate of nominal composition $YBa_2Cu_3O_7$. This is for ease of exposition only, and does not imply a limitation of the inventive method to that system.

Brief Description of the Drawings

FIG. 1 is a schematic phase diagram, depicting a cross section of a tentative ternary phase diagram of the Y_2O_3-BaO-CuO system;

FIG. 2 schematically depicts the cross section of an exemplary wire according to the invention;

FIG. 3 schematically shows a further exemplary embodiment of the invention; and

FIG. 4 schematically depicts exemplary apparatus according to the invention, namely, a superconducting solenoid.

FIGS. 5 and 6 show photomicrographs of a superconductor prepared by the prior art technique and prepared according to the invention, respectively;

FIGS. 7 and 8 similarly show a scanning electron fractograph of prior art superconductive material and material prepared according to the invention, respectively;

FIGS. 9, 10 and 11 show a low magnification photomicrograph and two high magnification micrographs, respectively, of a further superconductive sample according to the invention; and

FIG. 12 represents a collection of data on J_c as a function of magnetic field, for $YBa_2Cu_3O_{9-\delta}$ in a variety of (prior art) forms, and also produced according to the invention.

Detailed Description of Some Embodiments

Tentative ternary phase diagrams of the Y_2O_3-BaO-CuO system have recently been reported. See, for instance, K. G. Frase et al, "Phase Compatibilities in the System Y_2O_3-BaO-CuO at 950°C," Communications of the American Ceramic Society, Vol. 70(9) pp. C-204-205 (September 1987). FIG. 1 shows a tentative partial schematic phase diagram, derived from the above-referred to ternary phase diagram, that illustrates some aspects of the invention. As will be understood by those skilled in the art, the phase diagram is a schematic cross section of the ternary diagram along the tie-line of non-superconducting BaY_2CuO_5 and superconducting $Ba_2YCu_3O_7$. It will also be appreciated that further research may require modification of the phase diagram.

Compositions in fields 10, 11 and 12 of FIG. 1 are mixed solid phases (consisting of $BaY_2CuO_5/Ba_2YCu_3O_7$ and $Ba_2YCu_3O_7/BaCuO_2/CuO$, respectively. Compositions in field 13 are liquid + solid (the solid being BaY_2CuO_5). Finally, compositions in field 14 are single phase liquid. As is well known, the presently known high T_c superconductive phase in the Ba-Y-Cu-O system has nominal composition $Ba_2YCu_3O_7$.

(The optimal oxygen content is not necessarily equal to 7 but may differ slightly therefrom, e.g., 6.9. We intend to include such minor departures within the above nominal composition.)

Heating a sample of material of composition $Ba_2YCu_3O_7$ above the solidus line 17 (about 980°C in air or about 1010°C in oxygen) results in (partial or complete) melting. For instance, if the sample is heated to a temperature in field 13 of FIG. 1 (e.g., corresponding to point 15) then partial melting occurs, with the equilibrium compositions of the liquid and solid portions determined by the familiar lever rule. On the other hand, the equilibrium phase in field 14 of FIG. 1 is a uniform liquid. However, relatively slow heating through field 13 produces enrichment of the solid phase with Y, with attendant undesirable increase in the melting temperature. Consequently, in at least some of the embodiments of the invention it is considered advantageous to raise the temperature of the starting material relatively rapidly at least through field 13 to a temperature in field 14 (e.g., point 16). Exemplarily, the temperature is raised such that a sample of Ba-cuprate spends less than about 5 minutes (preferably less than 2 or even 0.5 minutes) in field 13 (or an equivalent solid-liquid region of an applicable phase diagram). In some cases it may be advantageous to permit establishment of thermal equilibrium by soaking the sample at a temperature close to but below the solidus, followed by rapid heating to the liquid region.

After being maintained in region 14 for a relatively non-critical period (typically long enough to ensure homogeneity of the melt and short enough to avoid undesired uptake [or possibly loss] of material by [from] the melt) at least a portion of the melt is rapidly cooled through field 13 (or an equivalent solid + liquid region of an applicable phase diagram) to a temperature (e.g., 18) below the solidus but above the orthorhombic/tetragonal transition temperature of $YBa_2Cu_3O_x$ at about 700°C. The cooling rate should be such that phase separation is substantially avoided or minimized. Exemplarily, the cooling rate through field 13 for a sample of Ba-cuprate is typically greater than about 100°C/min, and preferably greater than 200°C/min.

In many cases, it will be desirable to alter the shape of all or part of the molten material prior to its solidification, e.g., by drawing a fiber or a ribbon from the melt, by casting into a mold, or by extrusion through a die. The details of the shaping step as well as of the rapid cooling step depend, inter alia, on the desired shape of the superconductive body. For instance, a fiber or ribbon may be drawn or extruded by techniques of the type employed in the manufacture of optical fibers or of rapidly quenched glassy metals. The casting of bulk bodies will typically require cooling of the mold or die. The shape of the solidified body need not necessarily be the final shape of the superconductor, and at least in some cases it may be advantageous to carry out a separate solid state shaping step, e.g., hot forming at a temperature close to the solidus.

It may at times be advantageous to carry out the shaping of the superconductive material under conditions such that the material is in the solid + liquid region (field 13 of FIG. 1). In particular, the conditions can be chosen such that the solid + liquid mixture has an appropriate viscosity that allows easier shaping of the material. As will be readily appreciated, the processing time in the solid + liquid two phase region advantageously is kept to a minimum (exemplarily less then 10 minutes, preferably less than 1 minute) to reduce compositional separation. As discussed above, subsequent heat treatment should produce substantial homogenization.

Subsequent to the shaping and rapid solidification the body is typically heat treated so as to obtain material of the appropriate composition (e.g., oxygen content) and crystal structure and, possibly, to homogenize the material. Exemplarily, bodies made from the currently preferred Ba-cuprate (nominally composition $Ba_2YCu_3O_{6.9}$) can optionally be heat treated in oxygen (or an oxygen-containing atmosphere such as air) at a temperature in the range 850-950°C for a period in range 1-48 hours, typically followed by relatively slow cooling (e.g., average rate < 100°C/hour) in oxygen (or an oxygen-containing atmosphere to a temperature below about 300°C, so as to avoid formation of microcracks. Maintaining the sample at an intermediate temperature for some period (e.g., 10 minutes to 15 hours) many at times be advantageous, e.g., to facilitate attainment of the optimal oxygen content.

As will be appreciated, the details of the heat treatment will depend, inter alia, on the shape of the body. For instance, resolidified bodies having one or two relatively small dimensions (e.g., ribbons and fiber, respectively) may not require as extended post-solidification heat treatment as bulk bodies, since the diffusion distances (e.g., for O_2) are much smaller in the former cases than in the latter. Thus, it may be possible to carry out the heat treatment of fiber and/or ribbon as a continuous in-line process right after formation of the fiber or ribbon.

FIGS. 5 and 7 show a photomicrograph and a scanning electron fractograph of prior art sintered ceramic high T_c superconductive material (nominal composition $YBa_2Cu_3O_{6.9}$, having T_c of about 92K and J_c of about 700A/cm^2 at 77K and H=0). As can be seen from the Figures, the prior art material

is granular (average grain size substantially less than 10 μm) and porous, essentially without texture. FIGS. 6 and 8 show a corresponding micrograph and fractograph, respectively, of superconductive material produced according to the invention. The nominal composition of the material of FIGS. 6 and 8 is the same as that of the sintered material of FIGS. 5 and 7. The inventive material also has T_c of about 92K but has J_c of about 300A/cm^2 at 77K and H=0. The material according to the invention was produced by a process that comprises rapidly (within less than about 5 seconds) cooling the melt from about 1300°C to about 950°C, followed by a furnace cool to room temperature. As can be seen from FIGS. 6 and 8, the inventive process results in essentially 100% dense material that is strongly textured, with a substantial portion being relatively large elongate crystallites (e.g., having a long dimension that is typically greater than about 10μm, with aspect ratio typically 10:1 or greater, and with the long axis tending to lie in the basal plane of the orthorhombic superconductor), and that is predominantly single phase. The texture of the exemplary material is spherulitic. However, by providing for directional cooling macroscopically oriented growth can be obtained. Oriented growth (including spherulitic growth) typically results in a structure in which neighboring crystallites have similar orientations, with relatively low angle boundaries between adjacent crystallites. This is considered to be of significance in this layered material which has anisotropic superconductivity and thermal expansion, and may be an aspect that contributes to the improved J_c of material produced according to the invention, as compared to prior art sintered material.

A further embodiment of the inventive method is exemplified by FIGS. 9, 10 and 11, which show respectively a low and two high magnification photomicrographs of high T_c superconductive material produced according to the invention. The material was produced by maintaining a pressed and sintered sample of the starting material (powder of composition $YBa_2Cu_3O_x$) in the solid + liquid region (13 of FIG. 1) of the phase diagram (1 hour at 1030°C), followed by a furnace cool to room temperature, all under O_2. The resulting material had T_c of about 92K, and J_c of about 1700A/cm^2 at 77K and H=0.

In FIGS. 10 and 11 the needle-shaped crystallites are superconductive $YBa_2Cu_3O_7$, the rounded crystallites are non-superconducting Y_2BaCuO_5, and the bright phase is non-superconducting CuO(+BaO). The material thus is clearly not single phase (although more than 80% by volume typically is superconductive material), but the superconductive phase typically forms a continuous network. As FIG. 9 shows, the non-superconductive "bright" phase is non-homogeneously distributed, being concentrated mainly in thin regions between relatively large regions that are relatively free of the bright phase. FIG. 10 depicts a region that includes a "boundary" between two of the referred to large regions of FIG. 9, and FIG. 11 depicts a portion of the interior of one of the large regions.

FIG. 12 gives exemplary data of critical current density as a function of applied magnetic field, for samples of nominal composition $YBa_2Cu_3O_7$ produced by a variety of techniques. Line 120 represents bulk samples produced according to the invention. Prior art bulk samples (i.e., sintered) typically fall into region 121. The improvement in J_c, including the slower decrease of J_c with increasing magnetic field, is apparent from a comparison of 120 and 121. Line 122 pertains to single crystal samples. Line 123 pertains to thin film results. Further thin films have been found to have J_c (H=0) in the region indicated by bracket 124.

As FIG. 12 demonstrates, there exists a very large difference in J_c between polycrystalline bulk samples (especially prior art material, i.e., material with randomly oriented small grains) and single crystals and thin films. It is widely believed that this difference is due, at least in significant part, to grain boundary resistance effects. Such effects could be caused, inter alia, by the presence of inhomogeneities or impurities, mechanical defects (e.g., stress concentration or microcracks), altered stoichiometry (e.g., oxygen content), structural deviation, or crystal orientation change at grain boundaries. The presence of voids may also adversely affect the transport properties. These and/or possibly other effects are likely to result in low J_c regions at grain boundaries separating high J_c grains. Thus a treatment that eliminates or reduces these low J_c regions or perhaps increases the current carrying capacity of these regions could result in increased J_c of a bulk sample. We believe that the improved J_c observed in samples produced according to the invention is due to such an effect. In particular, the larger grain size and, significantly, the high degree of texture (with the attendant reduction in average orientation change at grain boundaries) are thought to at least contribute to the observed improvement. Other, so far unidentified factors, may of course also be contributing to the improvement.

The superconductive bodies produced according to the invention may be coated (e.g., for purpose of electrical or thermal stabilization, or mechanical or environmental protection) with a suitable material, e.g., a normal metal such as Ag, Cu, Zn, In, Cd, Al, Sn, etc. The coating can be applied by any suitable process, e.g., by evaporation, or by dipping in the molten metal. The bodies may also be coated with insulating material (e.g., polymers

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or some oxides), either alone or on top of metal coating. FIG. 2 schematically depicts in cross section an exemplary coated wire according to the invention, wherein 21 is the melted and resolidified high T_c ceramic superconductive material, and 22 is cladding material, exemplarily a metal cladding.

It is also envisaged to form a "wire" by a process substantially as described in the above referred to U.S. patent applications (Serial Numbers 036,160 and 046,825), except that the cladding material is a relatively ductile high melting point metal such as stainless steel, Nb or Ta (including a cladding consisting of ductile high melting point first metal matrix with second metal particles embedded therein, the second metal also having a high melting point and having substantially different chemical behaviour than the first metal, such that the second metal particles can be removed by selective etching), with typically a barrier layer on the inside of the cladding. After drawing the wire from a preform and, typically, shaping the wire such that it is at least approximately in its final form, the wire is heated (either all of it simultaneously or consecutively, e.g., by passing a hot zone along the length of wire) such that the oxide powder core of the wire melts, followed by resolidification and heat treatment.

In one exemplary embodiment the cladding is hermetically sealed such that all the O_2 that was given off by the oxide during melting and high temperature treatment is still available to re-oxidize the material at lower temperatures. In another exemplary embodiment O_2 is pumped into the wire from the wire ends through the voids that resulted from the densification of the oxide material upon melting and resolidification. And in still another exemplary embodiment the wire is made porous by selective etching of the second metal particles, and O_2 is supplied to the oxide through the porous cladding during the heat treatment.

The invention can be practiced in a number of ways. For instance, the material that is to be melted (the "charge") can be a sintered body or compressed powder pellet of superconductive oxide produced by a conventional technique, or the charge can be a mixture (in appropriate ratios) of the starting materials for oxide production (e.g., $BaCO_3$, Y_2O_3, and CuO powder, or nitrate, acetates, oxalates, etc., containing the desired metals). The composition of the charge can be such that the relevant metals (e.g., Y, Ba, and Cu) are present in the same ratio as they are found in the relative superconductive phase (e.g., 1:2:3), or the melt can be deficient in one (or more) of the metals, with the deficient metal(s) to be augmented in the melt. For instance, Y-deficient starting materials can be melted in a Y_2O_3-lined crucible, with Y being augmented from the crucible liner. Such a procedure typically will reduce the likelihood of poisoning of the melt. Furthermore, material once melted according to the invention can be re-melted, for instance, to facilitate further shaping or to eliminate trapped bubbles and/or other inhomogeneities. In some instances it may be advantageous to heat the charge slowly to a temperature below the liquidus (or to maintain the charge at that temperature for some period), followed by rapid heating into (and possibly through) the solid + liquid region. Such treatment may reduce oxygen evolution in the liquid material.

The charge can be melted in a crucible, contact-free (e.g., by torch, RF, electrical heater, or laser melting the end or middle of a suspended rod of the starting material), or such that the molten charge is in contact only with other charge material (e.g., by forming a molten puddle in a quantity of the starting material). Furthermore, a core of a first material (e.g., silver wire) can be coated with superconductive material (e.g., $Ba_2YCu_3O_7$ powder mixed with a binder, and possibly also with a metal powder such as Ag powder; the presence of the latter can improve the adhesion of the ceramic to the metal core. See the above referred to U.S. patent application Serial No. 046,825). The coated core is then moved through a heating zone such that the binder is driven off and at least the outer portion of the superconductive material coating is melted and rapidly resolidified, without substantial melting of the first material core. This can be accomplished by a variety of techniques, such as by means of circumferentially arranged lasers or electron beams, by means of a well controlled ring burner, or by microwave heating. FIG. 3 schematically depicts, in cross-sectional view, an exemplary body of the above described type, wherein 31 is the core (e.g., silver wire), 32 is the ceramic superconductive shell, with material outside of line 33 being resolidified (relatively dense) material, and material inside of 33 being less dense material, for instance, being in the sintered state. Layer 34 is a coating (exemplarily a polymer coating). It will be appreciated that 32 could in principle be completely resolidified superconductive material. The invention can also be practiced by forming a layer of precursor material (e.g., a $YBa_2Cu_3O_7$ layer produced by a prior art technique) on a substrate (e.g., ZrO_2), melting all or a portion of the precursor material, rapidly cooling the melted material below the solidus, followed by an appropriate heat treatment. The melting can be carried out by any appropriate means, including laser melting or by means of a heat lamp.

Another exemplary embodiment of the invention comprises casting superconductive slit lamellae of the type used in Bitter magnets, assembling a stack of lamellae, with appropriate insulator ma-

terial between neighboring lamellae, and with the lamellae arranged such that any given lamella overlaps with its neighboring lamella ro lamellae (thereby forming a continuous spiral), melting at least the overlap regions or otherwise establishing superconductive contact between the overlap regions, and heat treating the thus produced Bitter magnet as disclosed herein.

A toroidal superconductive magnet can also be formed by casting of the molten oxide into a tubular mold.

The inventive method typically can be used to fabricate high T_c superconductive bodies that are relatively dense throughout substantially all (typically < 95%) of the resolidified portion of the body. Bodies according to the invention typically have substantially greater fracture toughness than less dense identically shaped bodies of the same composition, fabricated by a prior art technique such as sintering of pressed powder. The latter frequently has densities in the range 70-85% of the theoretical density, depending on the heat treatment. The improvement in fracture toughness typically is at least about 50%. Inventive bodies typically also have critical currents that are substantially larger (exemplarily at least about 20% larger) than those of identically shaped prior art superconductive bodies of the same composition. The transition temperature T_c of bodies according to the invention can be identical to that obtainable in prior art bodies of the same composition. Some treatment conditions may lead to a slightly broadened transition, and materials produced according to the invention and having a somewhat broadened superconductive transition (but still reaching $R=0$ at or above 77K) are also contemplated.

Bodies according to the invention can be advantageously employed in a variety of apparatus and systems, e.g., those discussed in the previously referred to books by S. Foner and B. B. Schwartz. Exemplary of such applications is the superconductive solenoid schematically depicted in FIG. 4, wherein 41 is a clad superconductive wire according to the invention, and 42 is a tubular body that supports 41.

As disclosed above, zone melting is an exemplary technique that can usefully be employed in the practice of the instant invention. Indeed, zone melting is one of the techniques currently preferred by us.

One of the advantages of zone melting is the inherent presence of a temperature gradient which, typically, results in textured growth of the resolidified material. Furthermore, zone melting can be easily adapted for continuous processing, e.g., the manufacture of long lengths of wire or ribbon.

By "zone melting" we mean herein melting of a portion of the precursor material such that the liquid is in contact with solid precursor material. This is typically accomplished by forming a "hot zone" in the precursor material. The hot zone can be formed by any appropriate means, e.g., by means of a ring furnace or other localized furnace, by laser heating or induction heating. Typically, although not necessarily, the hot zone is caused to move relative to the quantity of precursor material, by moving the precursor material relative to the heat source, by moving the heat source relative to the quantity of precursor material or, possibly, by a combination of the two.

In an exemplary embodiment of the zone melting process an appropriate core member (e.g., a glass fiber or a metal wire) is coated with precursor oxide and the coated core member is moved relative to a localized heat source (e.g., a ring heater) such that a hot zone is caused to move along the coated core member. The core member can be coated by any appropriate technique, e.g., by application of a precursor-material-containing slurry or paste to the member, or by deposition of an adherent layer of precursor material (e.g., by reactive sputtering, evaporation, or precipitation from solution). Zone melting of the precursor coating is carried out such that at least the outer portion of the precursor coating is melted. Even though complete melting of the precursor coating is contemplated, partial melting is currently preferred (at least in conjunction with the use of core members such as SiO_2 fiber), since it decreases the possibility of adverse reaction of the superconductive oxide with the core member. If required (as, for instance, in the case of $YBa_2Cu_3O_x$), the resolidified precursor material is subjected to an appropriate oxygenation treatment, as will be appreciated by those skilled in the art.

In a further exemplary embodiment of the zone melting process, a long thin body of precursor material is surrounded by a normal metal (e.g., Ag) cladding, and a hot zone is caused to move along the composite body, with the conditions adjusted such that the precursor material in the hot zone melts whereas the metal cladding remains solid. This embodiment can be most advantageously used in conjunction with relatively low melting precursor material that is relatively stable with respect to oxygen loss. Exemplary of such materials are the superconductive members of the (Bi-Sr-Ca) copper oxide system (e.g., $BiSrCaCu_2O_8$ and $Bi_2Sr_2CaCu_2O_8$) and of the (Tl-Ba-Ca) copper oxide system (e.g., $Tl_2Ba_2CaCu_2O_8$).

Furthermore, it will be appreciated that the inventive method can also be practiced with unclad bodies of precursor material such as rods, wire, ribbon, or tape, as well as with thin films of precursor material formed on a planar substrate (including single crystal as well as polycrystalline or amor-

phous substrates). In the latter case, zone melting is considered to be particularly advantageous since it can result in a strongly textured superconductive film, with the elongate crystallites typically oriented with their c-axis normal to the substrates. This texture is likely to result in relatively high critical current densities.

In many cases it is advantageous to heat the precursor material such that the temperature of the molten portion of the material is below the liquidus, i.e., such that the material is in the solid + liquid field of the phase diagram. In addition to decreased possibility of "poisoning" of the melt by a substrate in contact therewith, the use of a melt temperature in the two-phase region also results in improved processing due to the higher viscosity of the liquid in the two-phase region, as compared to the melt above the liquidus. Furthermore, we have found that directional solidification from the two-phase region can result in a highly textured solid, with greatly elongated grains, and with neighboring grains having very similar orientations.

Exemplarily, we have prepared bodies (nominally of composition $YBa_2Cu_3O_7$) by a conventional technique from $BaCO_3$, Y_2O_3, and CuO. The samples were then heated to a temperature in the two-phase (solid + liquid) field of the phase diagram (about 1050-1200°C), followed by directional solidification by cooling at rates between 10-300°C/hour in a temperature gradient (typically about 20-50°C/cm) to about 900°C, i.e., below the solidus (about 1010°C). This was followed by an appropriate oxygenation treatment (exemplarily cooling at about 10°C/hour to 400°C). This treatment can result in an essentially 100% dense and well aligned structure comprising as a major component long, needle-or plate-shape grains of $YBa_2Cu_3O_7$. Frequently, the needles are about 100-3000 μm long and about 5-20 μm wide, with the needle axis coinciding with the a or b crystal lattice direction.

The needles are sometimes separated by a layer of a non-superconducting second phase, preliminarily identified as a copper oxide. The presence of this second phase typically does not affect current flow parallel to the needle axis. Frequently, a third phase (believed to be of the Y_2BaCuO_5-type) is also present in material prepared as described. These extra phases typically do not significantly affect the superconducting properties of material prepared by a process that involves directional solidification, except for the volume fraction effect. Samples prepared as described have exhibited J_c of about 1.7×10^4 A/cm² at 77K and H=0, and J_c of about 4×10^3 A/cm² at 77K and H=1 Tesla. These J_c values are believed to be the highest values reported for bulk $YBa_2Cu_3O_7$ to date. The transition temperature of material prepared as described can be slightly higher than that of conventionally prepared (sintered) bulk material, and the width of the transition typically is slightly reduced.

In a further embodiment of the inventive method pre-aligned precursor material is partially melted such that a portion of at least some grains of precursor material remains solid. These unmelted portions can then serve as solidification nuclei, resulting in textured growth. Alignment of the precursor material powder can be accomplished by any appropriate technique, e.g., by means of a magnetic field, pressure, or mechanically. See, for instance, J. W. Ekin, Advances in Ceramic Materials, Vol. 2 page 586 (1987). The aligned precursor material can be (but need not be) sintered prior to the partial melting. Solidification of the partially melted precursor material can be (but need not be) in a temperature gradient. It is considered advantageous to heat the precursor material to a temperature in the two-phase (liquid + solid) field of the phase diagram. Inter alia, this will result in a relatively slower melt process, as compared to material heated above the liquidus. Alternatively, a low melting point flux (e.g., CuO) can be added to the precursor material to facilitate fusion even at temperatures below the solidus. The heating can be carried out by any appropriate technique, including a volume heating technique such as induction heating.

Example I:

Powder of nominal composition $Ba_2YCu_3O_7$ and approximately 5 μm average diameter was prepared in a conventional manner (see, for instance, R. J. Cava et al, op. cit.), and pressed into a 3.1x3.1x31 mm pellet. The pellet was heated such that its central portion melted. Melting and drawing apart of the solid end portions resulted in formation of an elongated necked-down region whose minimum diameter was about 1.25 mm. After rapid solidification of the molten portion the sample was heat treated in oxygen (16 hours at 900°C; furnace cooled to 600°C; 2 hours at 600°C; furnace cooled to 250°C). The solidified portion of the sample was found to be superconductive, with transition onset temperature of about 98K, and completion (R=0) at 92K. The normalized magnetic susceptibility transition behavior of the resolidified material was essentially the same as that of an unmelted comparison sample of identical composition. In particular, the superconductive transition in both samples was substantially complete at 90K.

Example II:

Ba-cuprate powder as described in Example I was mixed with 17% by volume of Ag powder (1.3 μm average diameter). To the mixture was added 50% b.v. of a commercial acrylic binder (Cladan No. 73140 obtained from Cladan, Inc., San Marcos, California) dissolved in 1,1,1 trichloroethane. A 0.25 mm diameter Ag wire was dipped into the thus produced slurry. The coated wire was heat treated for 16 hours at 900°C in O_2, followed by furnace cooling to room temperature. The resulting wire preform had a diameter of about 0.75 mm, a superconductive transition temperature (R=0) of about 92K, and a critical current density of about 100A/cm² at 77K. The preform wire was then heated so that at least the outer portion of the ceramic coating was melted rapidly while substantially maintaining the geometry, followed by rapid cooling and resolidification. The wire was then heat treated substantially as described in Example I. The thus produced wire had a substantially 100% dense outer ceramic layer that adhered well to the Ag core, T_c (R=0) of 91K, and a critical current density of about 400A/cm².

Example III:

A ceramic-coated wire was produced substantially as described in Example II. The wire was then dipped into molten In, resulting in formation of a 0.125 mm thick In coating. The wire was superconducting, with T_c of about 92K.

Example IV:

A sintered pellet of $Ba_2YCu_3O_7$ powder, produced in the conventional manner, was rapidly heated above the liquidus, and a drop (approximately 6 mm diameter) of the melt caused to fall on a 40° inclined steel plate. At the moment of impact the drop was flattened into ribbon shape by dropping a steel block onto it. The contacting surface of the steel block carried a grooved pattern (1.25 mm pitch, 0.375 mm depth). The resulting patterned ribbon was about 0.75 mm thick. The ribbon was heat treated for 16 hours at 900°C, furnace cooled to 600°C, maintained for 2 hours at 600°C, then furnace cooled to 200°C, all in O_2. The resulting ribbon had T_c (R=0) of about 92K, and J_c of about 200A/cm² at 77K. It was substantially 100% dense, appeared to be essentially single phase, and its fracture toughness is at least 50% greater than that of a sintered test body of identical shape and composition.

Example V:

A rod is produced from $Ba_2YCu_3O_7$ powder by pressing in a conventional manner. The rod is heated such that a puddle of molten material is formed on the upper end of the rod, the melt is contacted with a silver-coated stainless steel bait rod wire, and the bait rod is withdrawn at a rate such that a 0.125 mm diameter fiber of the ceramic compound is continuously formed. The thus formed substantially 100% dense ceramic fiber is wound on a 1 m diameter spool with Ag-coated surface, and heat treated on the spool substantially as described in Example I. The heat treated fiber is coated by drawing it through molten Cd. The coated fiber has T_c of about 93K, and is wound on a tubular mandrel (having 1 m outer diameter), thereby producing a superconducting solenoid.

Example VI:

A substantially 100% dense ribbon (0.125 x 1.25 mm cross section) of nominal composition $Ba_2YCu_3O_7$ is formed in continuous manner by melt spinning, i.e., by causing a continuous stream of the molten material to fall onto a spinning ceramic-coated wheel maintained at about 400°C. After heat treatment substantially as described in Example I the ribbon is substantially single phase material and has T_c of about 92K.

Example VII:

Powder as described in Example I was pressed into a 2x2x30 mm pellet, the single phase pellet heated to 950°C, followed by rapid (about 200°C/min) heating to about 1300°C, and held at that temperature for about 2 minutes. The resulting single phase liquid was then rapidly cooled (about 200°C/min) to about 950°C, held at that temperature for 20 minutes, followed by furnace cooling to room temperature. All of the heat treatment was carried out in O_2 at ambient pressure. The sample was then given a homogenization and oxygen adjustment treatment as follows: heated to 920°C, soaked for 16 hours, cooled to 600°C at 100°C/hour, cooled to below 300°C at 20°C/hour, all in O_2 at ambient pressure. The sample had T_c (R=0) of 93K, and J_c (77K) at H=0, 50, 100, 200, and 10,000 gauss of 3100, 2300, 1320, 570, and 130 A/cm², respectively.

A prior art sample of identical composition and geometry (sintered at 920°C for 16 hours, furnace

cooled to room temperature, all in O_2) had T_c ($R=0$) of 92K, and J_c (77K) at 0, 50, 200 and 10,000 gauss of 570, 130, 20, and 3 A/cm^2, respectively.

Example VIII:

A pellet as in Example VII was heated to 1030°C, maintained at that temperature for 2 hours, and furnace cooled to room temperature, all in O_2. Subsequently, the sample was heated to 920°C, maintained at that temperature for 16 hours, followed by a furnace cool to room temperature, all in O_2. The material had T_c ($R=0$) of 93K, and J_c(77K) at 0, 50, 200, and 10,000 gauss of 1700, 1210, 310, and 100 A/cm^2, respectively.

Example IX:

A sample was prepared substantially as in Example VII, except that the pellet was maintained at 1030°C for only 20 minutes, followed by a rapid cool to 950°C, followed by a furnace cool to room temperature. The sample had T_c ($R=0$) of 91K and J_c (77K) at 0,200,and 10,000 gauss of 1600, 380, and 120 A/cm^2, respectively.

Example X:

A sample was prepared substantially as described in Example VII, except that the pellet was held at 1300°C for 5 minutes, then transferred rapidly (about 0.5 seconds) into a 980°C region of the furnace, and one end of the pellet exposed to a blast of O_2, leading to rapid cooling with directional solidification. The sample had T_c ($R=0$) of 92K and J_c (77K, $H=0$) of 7400 A/cm^2.

Example XI:

A 0.075 mm thick film of nominal composition $YBa_2Cu_3O_7$ is formed on a ZrO_2 substrate by coating a surface of the substrate with a slurry (containing about 30% by volume binder as in Example II, the remainder being $YBa_2Cu_3O_x$ powder), heating (50°C/hour) the coated substrate to 900°C to remove the binder, then raising the temperature to 950°C, maintaining it at that temperature for 2 hours, then rapidly (about 500°C/min) heating the precursor material by means of a heat lamp to 1300°C, maintaining this temperature for 10 seconds, then rapidly (100°C/min) cooling the melted precursor material to 950°C. The substrate with the solidified layer thereon is maintained at 950°C for 1 hour, then is slowly (30°C/hour) cooled to room temperature. All of the heat treatment is carried out in O_2 at ambient pressure. The thus produced superconductive film was T_c of 92K, and J_c ($H=0$) in excess of 1000 A/cm^2.

Example XII:

A thin rod of $YBa_2Cu_3O_{7-\delta}$ precursor material is made by a conventional technique. The rod is held vertically in a furnace, heated in oxygen to 900°C, and then slowly (10 cm/hr) dropped through a hot zone in the furnace, whereby a molten zone (1100°C) is caused to be moved through the rod. Subsequently, the rod is cooled slowly (10°C/hour) to 400°C. The resulting superconducting rod has a strongly textured structure, with many elongate grains aligned in the longitudinal direction, and has $J_c > 10^4$ A/cm^2 at 77K and zero field.

Example XIII:

A silver-coated steel wire is coated with $YBa_2Cu_3O_{7-\delta}$ precursor material in a conventional manner. The coated wire is then pulled under O_2 through a ring heater, with the heater power and pull speed adjusted such that a zone of molten precursor material is moved along the wire, with only the outer portion of the coating being molten (1050°C). Subsequent to the directional solidification of the precursor material the coated wire is cooled slowly (10°C/hour) in O_2 to 400°C. The resulting wire shows strong texture and has $J_c >$ 1000 A/cm^2 at 77K.

Example XIV:

On a Si wafer coated with a thin layer of polycrystalline zirconia is formed a layer of $YBa_2Cu_3O_7$ precursor material by a conventional process. The combination is heated to 900°C in O_2. A narrow hot zone is produced in the precursor layer by means of a line-focussed high intensity lamp, and the hot zone is moved (1 mm/sec) across the wafer. The conditions are adjusted such that the top portion of the precursor layer in the hot zone melts (1080°C), with the remainder of the material being solid. After completion of the zone melting/directional resolidification the wafer is slowly cooled to O_2 from 900°C to 400°C. The thus produced superconductive layer is strongly textured (c-axis preferentially normal to the substrate, many crystallites highly elongate in the scan direction) and has $J_c >$ 1000 A/cm^2 at 77K.

Example XV:

A "green" tape containing oriented $DyBa_2Cu_3O_7$ precursor material is formed by a standard "doctor blade" technique in a magnetic field of 5 Tesla normal to the tape, resulting in alignment of the particles with c-axis normal to the plane of the tape. The green tape is wound on a mandrel into a solenoid geometry, then heat treated and sintered in standard fashion. The sintered tape is then heated such that the material partially melts, with part of some of the grains remaining solid. Cooling of the molten portion below the solidus results in re-growth of the precursor material, with the partially melted grains serving as nuclei. The re-solidified tape is essentially 100% dense and contains relatively large grains that exhibit preferential orientation.

Claims

1. A method of fabricating an article comprising a quantity of a superconductive oxide, the method comprising

a) providing a quantity of oxide precursor material;

b) heating the precursor material; and

c) completing fabricating the article, the article comprising the heat treated precursor material, at least a portion thereof being superconductive;

CHARACTERIZED IN THAT

d) step b) comprises heating the precursor material such that at least a part thereof becomes a liquid, and causing the at least part of the precursor material to resolidify.

2. Method of claim 1, wherein step c) comprises heat treating the resolidified material in an oxygen-containing atmosphere such that the resolidified material becomes the superconductive oxide.

3. Method of any of claims 1 and 2, wherein step b) comprises producing a hot zone in the precursor material and causing the hot zone to move through at least part of the precursor material, with at least a part of the precursor material in the hot zone being liquid.

4. Method of any of claims 1-3, wherein associated with the precursor material is a phase diagram comprising a solid + liquid field, and step b) is carried out such that the at least part of the precursor material is in the solid + liquid field of the phase diagram.

5. Method of claim 3, wherein the precursor material is deposited on a filamentary or ribbon-like substrate and the precursor-covered substrate is moved relative to a stationary heat source, or the precursor material is deposited on a substantially planar substrate and the hot zone is caused to move relative to the stationary precursor-covered substrate, or the precursor material is surrounded by a normal metal cladding.

6. Method of any of claims 1-5, wherein solidification of the liquid precursor material is directional solidification carried out such that at least a substantial portion of the resolidified material comprises elongate crystallites, associated with each elongate crystallite being a long axis, at least a substantial fraction of the elongate crystallites measuring at least about 10µm along the long axis, and wherein in any given region of the resolidified material the elongate crystallites have similar orientation, with the long axis of any given elongate crystallite pointing in approximately the same direction as the long axes of the elongate crystallites that are adjacent to the given crystallite.

7. Method of any of claims 1-5, wherein the precursor material comprises particles, associated with each particle being a crystal lattice and a first crystal axis, step a) comprises causing the particles to be preferentially oriented such that the first crystal axes of at least a substantial fraction of the particles are approximately parallel, and step b) comprises heating the precursor material such that at least some of the preferentially oriented particles are only partially melted, whereby the resolidified material is caused to have a preferential crystal orientation.

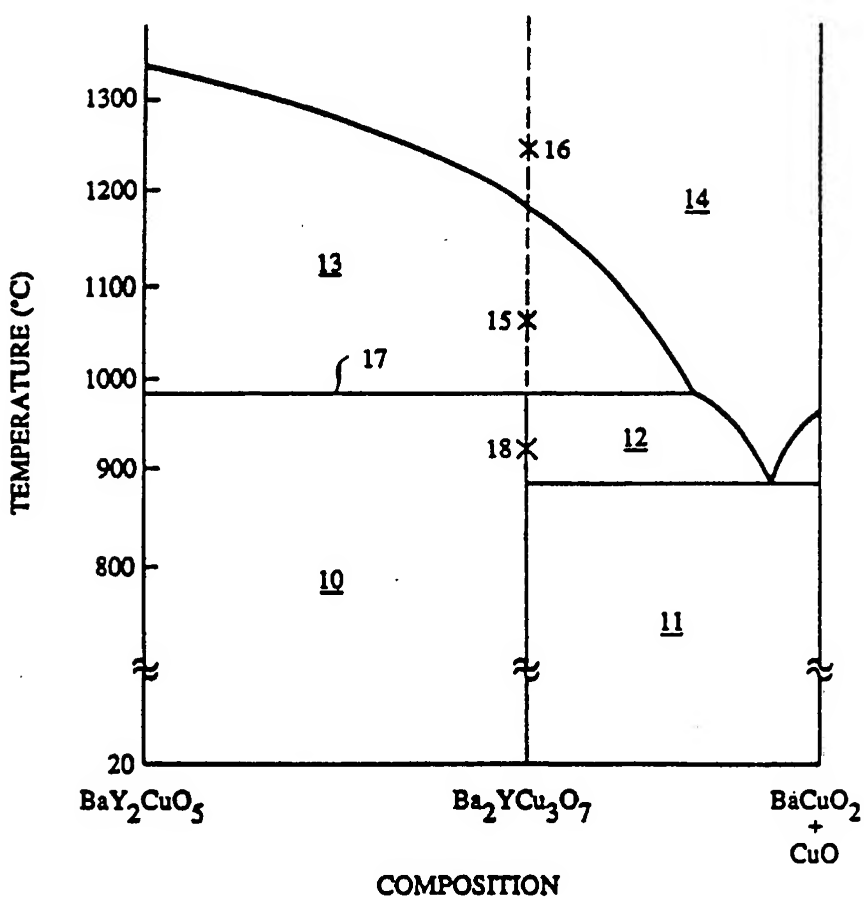
8. Method of any of claims 1-7, comprising providing a precursor material whose composition is essentially the same as the composition of the superconductive oxide, but not precluding a difference in the oxygen content of the precursor material and the superconductive oxide.

9. Method of any of claims 1-8, wherein the superconductive oxide is selected from the group consisting of the Ba-copper oxides, the La-copper oxides, the (Bi-Sr-Ca) copper oxides, and the (Tl-Ba-Ca) copper oxides.

10. Method of any of claims 1 and 5-9, comprising mixing Ag particles with the precursor material.

11. Use of an article fabricated according to any of claims 1-10 in an apparatus whose functioning depends on the presence of the superconductive oxide material.

FIG. 1


TEMPERATURE (°C)
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1200
1100
1000
900
800
20
16
14
13
15
17
18
12
10
11
BaY_2CuO_5
$Ba_2YCu_3O_7$
$BaCuO_2$ + CuO
COMPOSITION

FIG. 2

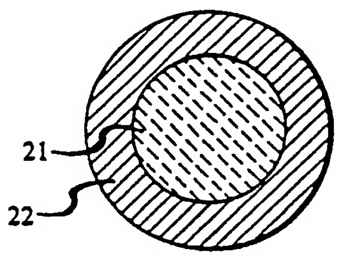


FIG. 3

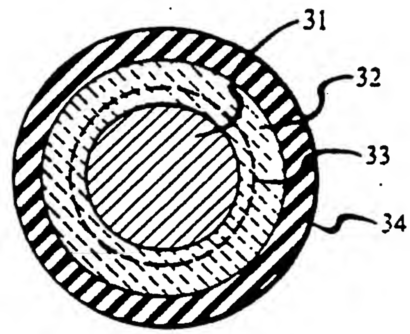


FIG. 4

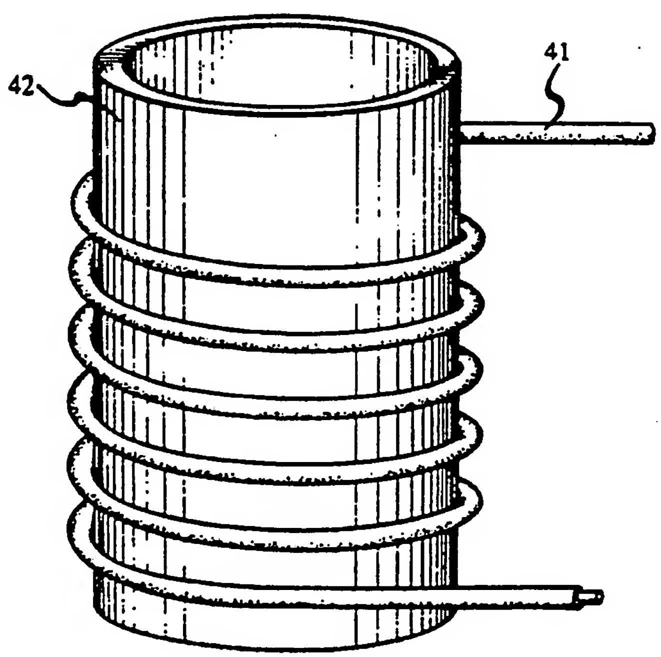
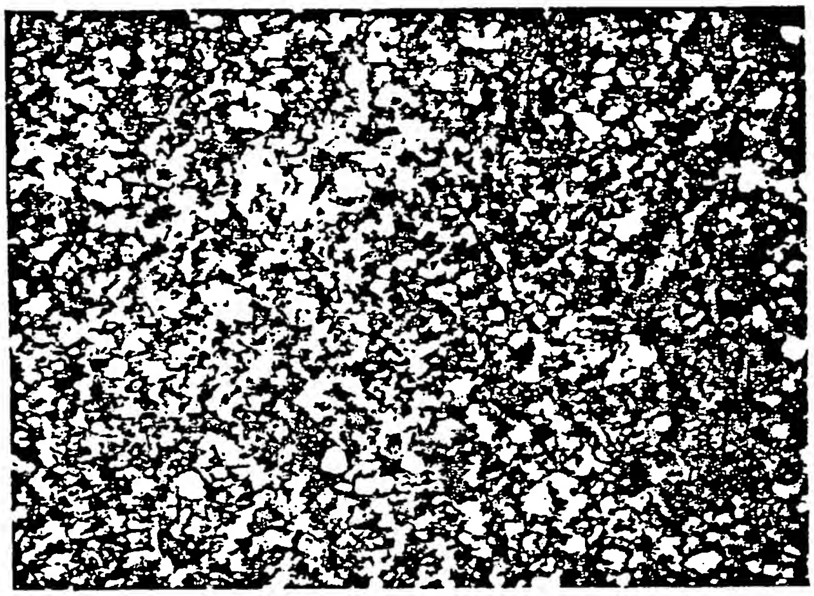
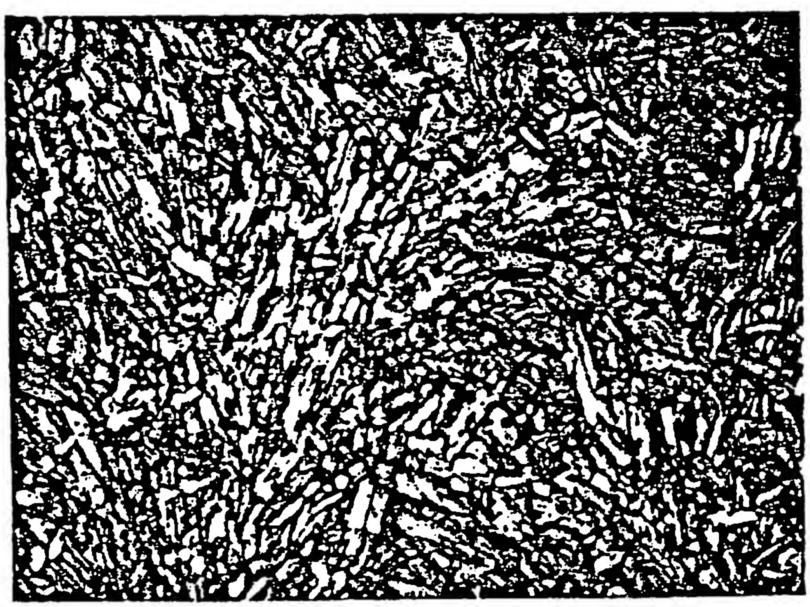


FIG. 5



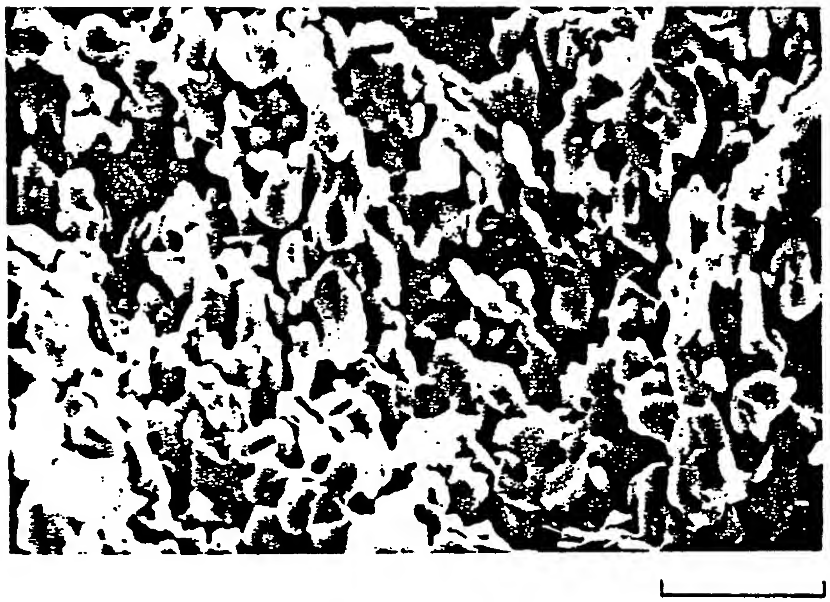
40 μm

FIG. 6



40 μm

FIG. 7



10 μm

FIG. 8

10 μm

FIG. 9

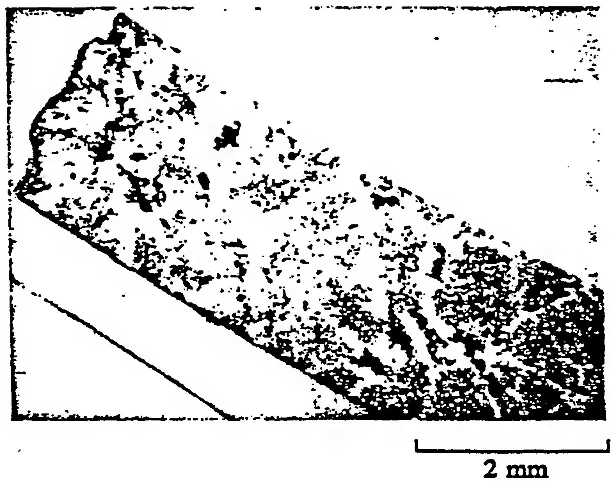
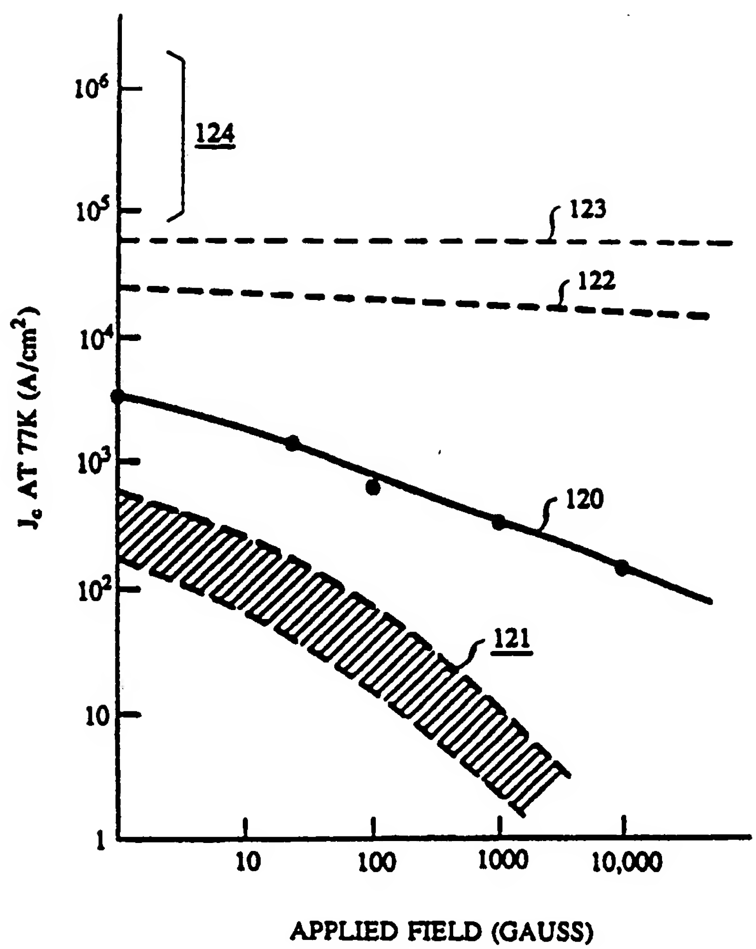


FIG. 10

FIG. 11

FIG. 12



10^6
10^5
10^4
10^3
10^2
10
1
124
123
122
120
121
J_c AT 77K (A/cm^2)
10
100
1000
10,000
APPLIED FIELD (GAUSS)